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EPR and optical spectroscopy of the Tm^{2+} ion in the $KMgF_3$ single crystal

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ABSTRACT

Paramagnetic Tm^{2+} ion centers in the $KMgF_3$ single crystal have been studied by electron paramagnetic resonance and optical spectroscopy. The Stark level energies of the cubic Tm^{2+} multiplets have been established from the luminescence spectra and the crystal field parameters have been calculated. Information about the phonon spectra of $KMgF_3$ crystals has been obtained from the electron-vibrational structure of the optical luminescence spectra.

1. Introduction

The rare-earth ions with the f^n-electron configuration are of great importance in connection with the development of solid-state devices such as lasers, scintillators and displays. The most common valence state of lanthanides in solids is the trivalent state. Some rare-earth ions may be stabilized in the divalent valence state and their properties are studied insufficiently. This work presents the results of electron paramagnetic resonance (EPR) and optical spectroscopy investigations of the Tm^{2+} ion in the $KMgF_3$ single crystal. Earlier, EPR and electron–nuclear double resonance (ENDOR) studies of the cubic symmetry Tm^{2+} center (T_c) were performed in Refs. [1,2], respectively. It was established that this center is in the Mg^{2+} position, i.e., it is in the octahedral coordination [2]. Moreover, to the best of our knowledge the optical spectroscopy data for the cubic Tm^{2+} ion in the sixfold coordination are presented for the first time. It should be noted that the divalent thulium ion was intensively studied in chloride compounds [3–7] in a similar coordination but no spectroscopic data are present in these works.

Thulium-doped $KMgF_3$ crystals were grown by the Czochralski method in the helium atmosphere at an excess pressure of 2.5 atm. Thulium ions were introduced into the initial charge as TmF_3 salts in the amount of 7 wt%. The charge was synthesized from the carefully dehydrated KF and MgF_2 salts in the ratio 52:48. LiF in the amount of 3 wt% was introduced as a charge compensator. The extending speed was 6 mm/h. To transfer thulium ions to the divalent state, the crystals were subjected to the γ-radiation for several hours at room temperature.

EPR spectra were measured on a modified ERS-231 spectrometer (Germany) [8] at the temperatures of 4.2 and 7–20 K. Optical spectra were measured on a multi-functional spectrometer [9] at $T=2$ and 77 K. A high-pressure xenon lamp with the power of 1 kW served as the source of the luminescence excitation. Cooled photoelectron multipliers (FEU-100, FEU-83) and germanium photodiode were used as detectors for the spectral regions of 300–1200 and 1000–1500 nm, respectively.

2. Experimental results

Three types of centers, Tm^{2+} (I), Tm^{2+} (II) and Nd^{3+}, located in different structurally inequivalent positions were separated in the synthesized $KMgF_3$. Nd^{3+} ions are present as a non-controllable admixture. It was established from the angular dependences of EPR lines in the (0 0 1) and (1 $\bar{1}$ 0) planes of the crystal (Fig. 1) that Tm^{2+}(I) has a cubic symmetry—T_c whereas Tm^{2+} (II) and Nd^{3+} consist of six magnetically inequivalent complexes with rhombic symmetry (Figs. 1 and 2). The intensity of the EPR lines of the rhombic Tm^{2+} is much less than those of the cubic ones. It should be noted that the angular dependence of rhombic Nd^{3+} is rather unusual, and at the initial moment it was masked as an

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